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Growth of Diameter-Controlled Zno Nanorod Arrays by Hydrothermal Technique for Polymer Solar Cell Application

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Abstract

Well-aligned ZnO nanorod arrays (ZNAs) grown on the ZnO seed layers coated ITO substrates ranging in various times from 1.5 to 5 hr have been fabricated from aqueous solutions at low temperature. Morphologies, crystalline structure and optical transmission of as-prepared ZNAs were investigated by a scanning electron microscope (SEM), X-ray diffraction (XRD) and UV-Visible transmission spectra, respectively. The results showed that ZNAs grew vertically from the substrates, having uniform diameter and length distribution, the average diameters of ZnO nanorods increased with increasing growth time when growth time was less than 3 hr. The XRD results showed that ZnO nanorods were wurtzite-structured (hexagonal) ZnO. The high optical transmission in the visible region for ZNAs grown in 1.5 hr was also found. Moreover, we fabricated a solar cell, and a PCE of 0.47% was achieved.

Keywords: ZnO nanorod arrays; Aqueous solutions; low temperature; optical transmission; polymer solar cell.Introduction

1. Introduction

Zinc oxide (ZnO), an important functional inorganic semiconductive material, has a direct wide bandgap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV. In recent years, it has attracted considerable attention due to its distinguished performance and potential applications for optoelectronic and electronic applications [1]. Recently, nanostructured materials have extensively been studied for practical applications [2], [3]. Great progress in nanostructured ZnO with diverse morphologies such as nanorods, nanowires, nanobelts and nanotubes has been made [4]-[6]. In particular, well-aligned ZNAs are highly desirable for their potential applications as electroluminescent devices [7], [8], field emission devices [9], solar cells [11]-[13] and nanogenerators [14]. Up till now, a number of

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physical and chemical techniques such as the vapour liquid solid method [8], chemical vapour deposition [9], and hydrothermal growth [10]-[13] were used to fabricate well-aligned ZnO nanorod arrays. Among these methods, the physical methods are expensive and time consuming. In contrast, hydrothermal grown ZNAs have recently attracted extensive interest because of their low growth temperatures (≤95 °C) and good potential for scale up [4], [10]-[13]. It is well known that the diameter of ZnO nanorod is of critical importance for the development of novel optoelectronic and electronic devices [15]. To the best of our knowledge, so far, many reports on fabrication and properties of well-aligned ZNAs have been found [16]-[23], however, few reports on diameter-controlled well-aligned ZnO nanorod arrays in detail [13].

In this work, we report a simple two-step process to grow diameter-controlled well-aligned ZNAs at low temperature (93 °C) on ITO substrates, the diameter of ZnO nanorods can be modulated simply by tailoring reaction time. In addition, the crystalline structure and optical transmission of well-aligned ZNAs were systematically investigated. Moreover, a solar cell with inverted structure ITO/ZNAs/P3HT: PCBM/MoO3/Ag was fabricated and investigated.

2. Experimental

2.1. Materials

In our experiments, Zinc acetate dehydrate [Zn $(CH_3COO)_2 \cdot 2H_2O$], zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$], hexamethylenetetramine (HMTA, $C_6H_{12}N_4$), ethanol and acetone were analytical reagent grade and used without further purification, they were purchased from Kelong Chemical Agent. Both regioregular poly (3-hexylthiophene-2,5-diyl) (P3HT, 99.5%) and (6,6)-phenyl C_{61} butyric acid methyl ester (PCBM, 99.5%) were purchased from Lumtec. All the aqueous solutions were prepared using distilled water (resistivity=18.2 MΩ·cm). ZNAs grew on the indium tin oxide coated glass substrates (ITO, 10 Ω/sq). The substrates were first cleaned by ultrasonic agitation in detergent, deionized water, acetone and ethanol, respectively. The cleaned substrates were then blown dry using nitrogen gas and treated with O_2 plasma for 5 min.

2.2. Preparation

Fabrication of ZnO seed layers: zinc acetate dehydrate [Zn $(CH_3COO)_2 \cdot 2H_2O$] was dissolved in ethanol with a concentration of 10 mM. A droplet of solution was coated onto treated ITO substrates, rinsed with clean ethanol after 10 s, and then blown dry with a stream of nitrogen gas. This coating step is repeated four times. The coated substrates were dried at room temperature and then annealed in air at 350 ºC for 20 min to yield layers of ZnO seed. The zinc acetate deposition and decomposition procedure is carried out twice to ensure a complete and uniform coverage of ZnO seeds.

Growth of well-aligned ZNAs: Well-aligned ZNAs were grown in 200 mL of equimolar (50 mM) aqueous solution of zinc nitrate hexahydrate [Zn $(NO_3)_2 \cdot 6H_2O$] and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) in a conventional reaction flask. The ITO substrates coated ZnO seed layers were immersed into the aqueous solution upside-down in the flask. The reaction temperature was 93 ºC. Growth time varied from 1.5 to 5 hr. After growth, the substrates were removed from the solution, rinsed with deionized water and dried at 50 °C in air.

Preparation of a solar cell: For the fabrication of inorganic/polymer hybrid solar cells with inverted structure, we selected ZNAs grown in 1.5 hr as the inorganic layer. The organic layers consisted of P3HT: PCBM (1:1 by weight) were spin-coated on the top of the ZNAs from a chlorobenzene solution with a concentration of 30 mg/mL in air, then annealed at 110 °C for 15 min under vacuum (≤133 Pa). The 3 nm thick MoO_3 was deposited on the P3HT: PCBM layers under a pressure of 2×10^{-3} Pa as a buffer layer [24]-[26], followed by the deposition of 200 nm thick Ag electrodes through a shadow mask.

2.3. Characterization

Morphologies of as-grown ZNAs were observed with a scanning electron microscope (SEM, JEOL, and JSM-5900LV). Optical transmission was measured with a UV-Vis spectrophotometer (SHIMADZU UV1700)., The crystalline structure of the nanorods was confirmed by X-ray diffraction (XRD) analysis using CuKα radiation of 0.154056 nm with a Philips X'pert Pro MPD diffractometer. The I-V characteristics of as-prepared solar cell in dark and under illumination were recorded by a Keithley 4200 programmable voltage-current source [27]-[29]. A light source integrated with xenon lamp with an illumination power of 100 mW/cm^2 was used as a solar simulator. All measurements were performed under ambient conditions without device encapsulation.

3. Results and discussion

Fig. 1 shows the typical scanning electron microscopy (SEM) images of the ZNAs grown at various times ranging from 1.5 to 5 hr. It can be seen that the ZnO nanorods uniformly covered the entire surface with the hexagonal cross section. From the cross section image, the nanorods grew vertically from the substrates, having uniform thickness and length distribution. The diameter and length of the nanorods grown in 1.5 hr (Fig. 1(a) and (b)) are 50-60 nm and 800 nm, respectively. When growth time of the nanorods increases to 3 hr, the diameter of nanorods increases to 90-110 nm (Fig. 1(c)), however, continuing to increase growth time of the nanorods to 5 hr, the diameter of nanorods is no more increase (Fig. 1(e)). Interestingly, increasing growth time of nanorods to 3 hr, the length of nanorods decreases to 450 nm (Fig. 1(d)), however, continuing to increase growth time of nanorods to 5 hr, the length of nanorods increases to 600 nm (Fig. 1(f)).

The XRD pattern of the ZNAs grown on the ZnO seeds/ITO substrates in 3 hr is shown in Fig. 2. It can be noted that besides diffraction peaks of ITO substrates, all of the diffraction peaks of ZnO nanorods can be indexed as those from the known wurtzite-structured (hexagonal) ZnO (JCPDS card No. 36-1451), the (002) diffraction peak of ZnO nanorods exhibits a substantially greater intensity, further confirming that ZnO nanorods are much better aligned on a ZnO seeds-coated ITO substrate and also that NRs grow along (0001) direction.

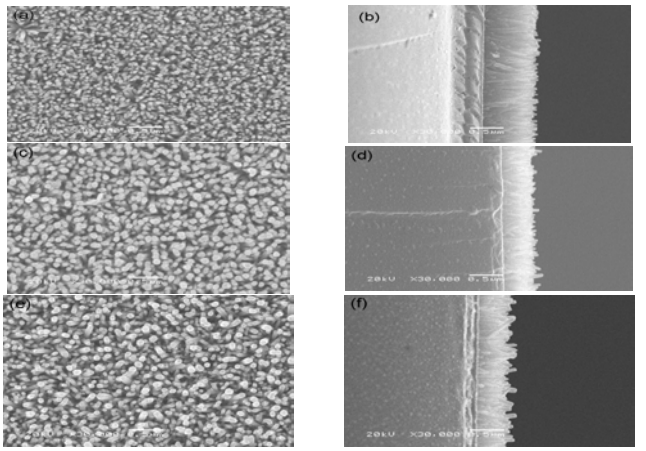

Fig. 1. Surface and cross-sectional SEM images of the ZNAs grown in various times, 1.5 hr ((a) and (b)), 3 hr ((c) and (d)) and 5 hr ((e) and (f)), respectively. All scale bars are 0.5 μm.

Fig. 3 shows the optical transmission of the well-aligned ZNAs grown in various times from 1.5 to 5 hr. The high optical transmission (>80%) in the visible for the well-aligned ZNAs grown in 1.5 hr was

obtained, such high optical transmission is attributed to wide bandgap and well-aligned growing on the substrate of ZnO nanorods uniformly. High optical transmission of ZNAs will be contributed to developing some high performance photoelectronic devices. It is evident that the optical transmittance decreases in the visible region with increasing growth time of the well-aligned ZNAs from 1.5 to 5 hr.

For the fabrication of inorganic/polymer hybrid solar cells with inverted structure, we select ZNAs grown in 1.5 hr as inorganic layer, Fig. 4 displays the typical current density-voltage (J-V) characteristics of solar cell in dark and under illumination. The device exhibits an open circuit voltage (V_{oc}) of 239 mV, a short circuit current (J_{sc}) of 5.07 mA/cm^2, a fill-factor (FF) of 39%, and a PCE of 0.47%.

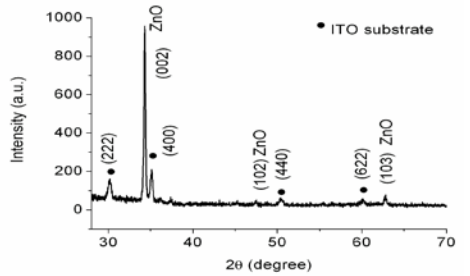

Fig. 2. The XRD pattern of well-aligned ZNAs grown in 3 hr on a ZnO seeds/ITO substrate.

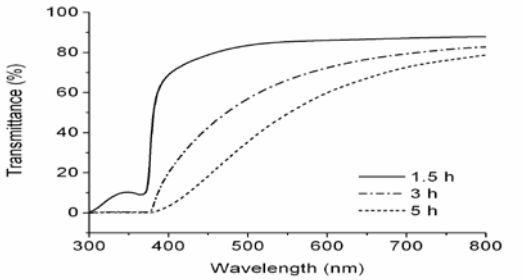

Fig. 3. Optical transmission of the well-aligned ZNAs grew in various times.

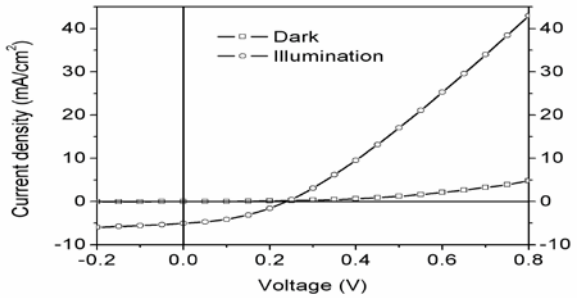

Fig. 4. Current density-Voltage (J-V) characteristics of ITO/ZNAs/P3HT: PCBM/MoO_3 (3 nm)/Ag (200 nm) solar device in dark and under AM1.5 illumination with an intensity of 100 mW/cm^2.

4. Conclusions

In summary, the well-aligned ZNAs grown on the ZnO seeds/ITO substrates in various times from 1.5 to 5 hr were fabricated. The ZnO nanorods grew vertically from the substrates, having uniform thickness and length distribution. We found that the diameter of ZnO nanorods increased with increasing growth time below 3 hr. The high optical transmission in the visible for the well-aligned ZNAs grown in 1.5 hr was obtained; such high optical transmission is attributed to wide bandgap and vertical growing on the

substrate of ZnO nanorods uniformly. Furthermore, we fabricated a solar cell, and a PCE of 0.47% was achieved.

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References

[1] H. Zhu, C.-X. Shan, J.-Y. Zhang, Z.-Z. Zhang, B.-H. Li, D.-X. Zhao, B. Yao, D.-Z. Shen, X.-W. Fan, Z.-K. Tang, X. Hou, and K.-L. Choy, "Low-threshold electrically pumped random lasers," *Adv. Mater.*, vol. 22, pp. 1-5, Jan. 2010.

[2] Z. L. Yuan, S. L. Tao, J. S. Yu and Y. D. Jiang, "Optical properties of 4-(Dicyanomethylidene)-6-(4-dimethylaminostyryl)-2-methyl-4H-pyran nanoparticles prepared by reprecipitation," *Chem. Lett.*, vol. 39, pp. 302-303, Mar. 2010.

[3] J. S. Yu, Z. L. Yuan, G. Z. Xie and Y. D. Jiang, "Preparation, properties, and applications of low-dimensional molecular organic nanomaterials," *Journal of Electronic Science and Technology*, vol. 8, pp. 3-9, Mar. 2010.

[4] B. Liu and H. C. Zeng, "Room temperature solution synthesis of monodispersed single-crystalline ZnO nanorods and derived hierarchical nanostructures,' *Langmuir*, vol. 20, pp. 4196-4204, Feb. 2004.

[5] Z. W. Pan, Z. R. Dai and Z. L. Wang, "Nanobelts of semiconducting oxides," *Science*, vol. 291, pp. 1947, Feb. 2001.

[6] Y. Xi, J. Song, S. Xu, R. Yang, Z. Gao, C. Hu and Z. L. Wang, "Growth of ZnO nanotube arrays and nanotube based piezoelectric nanogenerators," *J. Mater. Chem.*, vol. 19, pp. 9260-9264, Oct. 2009.

[7] R. Konenkamp, R. C. Word and C. Schlegel, "Vertical nanowire light-emitting di ode," *Appl. Phys.Lett.*, vol. 85, pp. 6004-6006, Oct. 2004.

[8] W. I. Park and G. C. Yi, "Electroluminescence in n-ZnO nanorod arrays vertically grown on p-GaN," *Adv. Mater.*, vol. 16, pp. 87-90, Sep. 2004.

[9] L. M. Li, Z. F. Du, C. C. Li, J. Zhang and T. H. Wang, "Ultralow threshold field emission from ZnO nanorod arrays grown on ZnO film at low temperature," *Nanotechnology*, vol. 18, pp. 355606, Aug. 2007.

[10] L. Vayssieres, "Growth of arrayed nanorods and nanowires of ZnO from aqueous solutions," *Adv. Mater.*, vol. 15, pp. 464-466, Mar. 2003.

[11] H. Q. Le, S. J. Chua, Y. W. Koh, K. P. Loh, Z. Chen, C. V. Thompson and E. A. Fitzgerald, "Growth of single crystal ZnO nanorods on GaN using an aqueous solution method," *Appl. Phys. Lett.*, vol. 87, pp. 101908, Sep. 2005.

[12] L. Vayssieres, K. Keis, S.-E. Lindquist and A. Hagfeldt, "Purpose-built anisotropic metal oxide material: 3D highly oriented microrod array of ZnO," *J. Phys. Chem. B*, vol. 105, pp. 3350-3352, May 2001.

[13] L. E. Greene, M. Law, J. Goldberger, F. Kim, J. C. Johnson, Y. Zhang, R. J. Saykally and P. D. Yang, "Low-temperature wafer-scale production of ZnO nanowire arrays," *Angew. Chem. Int. Ed.*, vol. 42, pp. 3031-3034, Mar. 2003.

[14] Z. L. Wang and J. Song, "Piezoelectric nanogenerators based on zinc oxide nanowire arrays," *Science*, vol. 312, pp. 242-246, Apr. 2006.

[15] B. Kannan, K. Castelino and A. Majumdar, "Design of nanostructured heterojunction polymer photovoltaic devices," *Nano* Lett., vol. 3, pp. 1729-133, Nov. 2003.

[16] S. F. Yu, C. Yuen and S. P. Lau, "Random laser action in ZnO nanorod arrays embedded in ZnO epilayers," *Appl. Phys. Lett.*, vol. 84, pp. 3241-3243, Apr. 2004.

[17] H. M. Zhang, X. Quan, S. Chen and H. M. Zhao, "Fabrication of needle-like ZnO nanorods arrays by a low-temperature seed-layer growth approach in solution," *Appl. Phys. A*, vol. 89, pp. 673-679, July 2007.

[18] H. Chik, J. Liang, S. G. Cloutier, N. Kouklin and J. M. Xu, "Periodic array of uniform ZnO nanorods by second-order self-assembly," *Appl. Phys. Lett.*, vol. 84, pp. 3376-3378, Apr. 2004.

[19] S.-N. Bai and T.-Y. Tseng, "The structural and optical properties of ZnO nanowire arrays prepared by hydrothermal synthesis method," *J Mater Sci: Mater. Electron.*, vol. 20, pp. 604-608, July 2009.

[20] A. l. Yang and Z. L. Cui, "Controlling the orientation of ZnO nanorod arrays using TiO_2 thin film templates dip-coated by sol-gel," *Journal of Nanoparticle Research*, vol. 9, pp. 245-250, Sep. 2007.

[21] J. B. Cui, C. P. Daghlian, U. J. Gibson, R. Püsche, P. Geithner and L. Ley, "Low-temperature growth and field emission of ZnO nanowire arrays," *J. Appl. Phys.*, vol. 97, pp. 044315, Jan. 2005.

[22] J. Nayak, S. N. Sahu, J. Kasuya and S. Nozaki, "Effect of substrate on the structure and optical properties of ZnO nanorods," *J. Phys. D: Appl. Phys.*, vol. 41, pp. 115303, May 2008.

[23] H. S. Shin, J. I. Sohn, D. C. Kim, W. T. S. Huck, M. E. Welland, H. C. Choi and D. J. Kang, "Density control of ZnO nanowires grown using Au-PMMA nanoparticles and their growth behavior," Nanotechnology, vol. 20, pp. 085601, Feb. 2009.

[24] V. Shrotriya, G. Li, Y. Yao, C. W. Chu and Y. Yang, "Transition metal oxides as the buffer layer for polymer photovoltaic cells," *Appl. Phys. Lett.*, vol. 88, pp. 073508, Feb. 2006.

[25] C. Tao, S. P. Ruan, X. D. Zhang, G. H. Xie, L. Shen, X. Z. Kong, W. Dong, C. X. Liu and W. Y. Chen, "Performance improvement of inverted polymer solar cells with different top electrodes by introducing a MoO3 buffer layer," *Appl. Phys. Lett.*, vol. 93, pp. 193307, Nov. 2008.

[26] V. Shrotriya, Y. Yao, G. Li and Y. Yang, "Effect of self-organization in polymer/fullerene bulk heterojunctions on solar cell performance," *Appl. Phys. Lett.*, vol. 89, pp. 063505, Aug. 2006.

[27] N. N. Wang, J. S, Yu, Y. Zang, J. Huang and Y. D. Jiang, "Effect of buffer layers on the performance of organic photovoltaic cells based on copper phthalocyanine and C60," Sol. Energy Mater. Sol. Cells, vol. 94, pp. 263-266, Oct. 2010.

[28] J. S. Yu, N. N. Wang, Y. Zang and Y. D. Jiang, "Organic photovoltaic cells based on TPBi as a cathode buffer layer," *Sol.* Energy Mater. Sol. Cells, vol. 95, pp. 664-668, Jan. 2011.

[29] J. Huang, J. S. Yu, Z. Q. Guan and Y. D. Jiang, "Improvement in open circuit voltage of organic solar cells by inserting a thin phosphorescent iridium complex layer," *Appl. Phys. Lett.*, vol. 97, pp. 143301, Oct. 2010.